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Influence of Cattle-Manure Slurry Application on the Solubility of Cadmium, Copper, and Zinc in a Manured Acidic, Loamy-Sand Soil

P. del Castillo,* W. J. Chardon, and W. Salomons

ABSTRACT

The concentrations of Cd, Cu, and Zn were evaluated bimonthly in the soil solution of five acidic loamy-sand soil plots during an 18-mo period, before and after application of 25 Mg ha⁻¹ cattle-manure slurry on top of the plots. pH, Cd, Zn, Cu, and Fe concentrations, electrical conductivity (EC), and dissolved organic carbon (DOC) were monitored in the soil-solution samples extracted from soil down to 80-cm depth. Dissolved metal concentrations ranged from 9×10^{-7} to 9×10^{-5} mmol m⁻³ for Cd, from 0.14 to 33 mmol m⁻³ for Zn, from 0.005 to 5 mmol m⁻³ for Cu, and from 0.54 to 4.6×10^3 mmol m⁻³ for Fe. Maximum soil solution concentrations of Cd (9×10^{-5} mmol m⁻³) and Zn (33 mmol m⁻³) were found between 0- and 40-cm depth 6 wk after cattle-manure slurry application; Cu and Fe concentrations were not elevated. Except for the peak concentrations of Cd and Zn following the cattle-manure slurry application, no statistically significant temporal trends in heavy metal concentrations were observed. Multiple linear regression analysis showed a positive correlation between the metal concentrations with DOC and a negative correlation with pH. High EC levels in topsoil layers, resulting from manuring were also found to increase metal concentrations. In the topsoil the Cd and Zn concentrations were affected by soil solution pH, and in the subsoil by DOC variations. The Cu concentration was affected by DOC variations in all soil layers. Supercentrifugation of selected subsoil samples from one sampling date removed 80% of the Cd, Zn, and Cu from the solution along with DOC and Fe. Cation-exchange column experiments as well as anodic stripping voltammetry measurements (speciation) of selected soil solution samples, showed that 30 to 70% of the dissolved Cu and all Cd was bound in relatively fast dissociating metal complexes. The observed variations in soil solution heavy metal concentration and speciation show that a distribution coefficient that describes the partition of metals over soil solution and solid phase is not a constant but depends on the physicochemical situation.

THE POTENTIAL TOXICITY of heavy metals in the environment depends on their concentration in the soil and soil solution, and dissociation kinetics of the dissolved species. Land disposal of waste materials such as sewage sludges and animal manure slurries may directly or indirectly alter the heavy metal status of the soil by affecting metal solubility or dissociation kinetics. The solubility of heavy metals in manured soils is of particular concern in the Netherlands and in other areas where animal manure slurries are applied in excess. This is worsened by the fact that in the past, pig feed contained high amounts of Cu and Zn as additives, resulting in an accumulation of these metals through the manuring of agricultural soils.

Much past research on the concentrations of heavy metals in the soil solution focused on sewage-sludge amended soils. Dissolved heavy metal concentrations show a wide range in sludge-amended soils: 2×10^{-4} to 0.2 mmol Cd m⁻³, 0.03 to 9 mmol Zn m⁻³, and 0.02 to 0.6 mmol Cu m⁻³ (Hodgson et al., 1965, 1966; Sidle and Kardos, 1977; Hinesly and Jones, 1977; Gerritse et al., 1983; Christensen, 1987). Concentrations as high as 1.3 mmol Cd m⁻³, 350 mmol Zn m⁻³ (Behel et al., 1983),

and 25 mmol Cu m⁻³ (Emmerich et al., 1982) have been observed. Soil properties affecting heavy metal solubility include pH (Buffle, 1988), DOC complexants such as fulvic acids (Mahler et al., 1980; Sposito et al., 1982; Boyle and Fuller, 1987) and lower molecular weight organic ligands (Pohlman and McColl, 1986, 1988), soil solution ionic strength (Salomons and Förstner, 1984; Boyle and Fuller, 1987) and the nature of sorbing soil surfaces (König et al., 1986).

Ten percent or less of the Cd in solution was found to be bound to organic ligands in a study with sludge-amended soils (Mahler et al., 1980). Low percentages were also found by Tills and Alloway (1983) in soils contaminated by mining or sewage sludge, and by Hirsh and Banin (1990) for unpolluted arid-zone forest soils. Only in a few studies, e.g., Gardiner (1974), Hirsch and Banin (1990), Sposito et al. (1982), and Tills and Alloway (1983) have field data been compared with results predicted by models.

The processes that affect heavy metal solubility may also influence heavy metal leaching in soils. Boyle and Fuller (1987) found that Zn leaching through soil columns was enhanced by elevating the DOC or ionic strength (*I*) of the percolating solution. Because animal manure slurries have a high ionic strength (*I* = 0.5) and contain significant amounts of easily degradable organic materials (Japenga and Harmsen, 1990; Bril and Salomons, 1990), manure slurry application to soil may be expected to have a significant effect on heavy metal solubility. The main purpose of the present study was to determine the effect of slurry application on Cd, Cu, and Zn concentrations in the soil solution, and to assess temporal variations in the concentrations of these metals in different field plots. In addition, Hesterberg et al. (1993) attempted to model the results of this study.

MATERIALS AND METHODS

Experimental Plots

In 1988 to 1989, the heavy metals in the soil solution were studied on five (10 by 100 m) acidic, loamy-sand soil plots at the Institute for Soil Fertility Research experimental farm in Haren, the Netherlands. The taxonomic classification of the soil is given by Hesterberg et al. (1993). The plots were artificially drained by a drainage tile at 1-m depth, the approximate depth of groundwater in winter. Before 1971, the plots were not used for experiments; from 1971 through 1987 all plots were subjected to conventional Dutch agricultural practices: crop rotations of forage maize (*Zea mays* L.), potatoes (*Solanum tuberosum* L.), and sugar beets (*Beta vulgaris* L.).

A principal difference between the plots was the constant annual fertilizer or pig-manure slurry application between 1971 and 1982 consisting of:

1. 40 Mg ha⁻¹ pig slurry (manure-40 plot), or
2. 80 Mg ha⁻¹ pig-manure slurry (manure-80 plot), or
3. 160 Mg ha⁻¹ pig-manure slurry (manure-160 plot), or

Abbreviations: EC, electrical conductivity; DOC, dissolved organic carbon; *I*, ionic strength; DPASV, differential pulse anodic stripping voltammetry; FAAS, flame atomic absorption spectrometry; TOC, total organic carbon; NaDDC, sodium diethyldithiocarbamate; MIBK, 4-methyl-2-pentanone; COD, chemical oxygen demand; ETAAS, electrothermal atomic absorption spectrometry.

DLO-Institute for Soil Fertility Research (IB-DLO), P.O. Box 30003, 9750 RA Haren, the Netherlands. Received 20 July 1992.
*Corresponding author.

4. a combination of mineral fertilizers [NH_4NO_3 + CaCO_3 (ammonium nitrate, limestone); $\text{Ca}(\text{H}_2\text{PO}_4)_2$ + CaSO_4 (superphosphate), and K_2SO_4 (potassium sulfate)], in dosages of N, P, and K equivalent to 40 Mg ha^{-1} pig manure slurry (fertilizer-40 plot), or
5. a combination of mineral fertilizers as in Treatment 4, but in rates equivalent to 80 Mg ha^{-1} pig manure slurry (fertilizer-80 plot).

An exception to these treatments was the application to the fertilizer plots, in 1975, of $\text{Ca}_3(\text{PO}_4)_2 \cdot x(\text{Ca}_2\text{SiO}_4)$ (basic slag, a byproduct from steel production, mainly consisting of silicocarnotite) as a phosphate source. All plots were limed with $\text{CaMg}(\text{CO}_3)_2$ (dolomite) in 1972 and 1975. Between 1982 and 1987, all plots received an annual fertilizer-40 treatment (4 above).

After the forage maize harvest in October 1987, the plant stubble was cut at ground level and left on the plots. The plots were kept fallow during the spring and summer of 1988 and 1989; weed control was carried out by hand several times.

Experimental Treatments

To determine the effect of dairy cattle-manure slurry on heavy metal solubility in the various plots, soil solution samples were collected and analyzed periodically (during a 14-mo period) before and after applying a single dose of 25 Mg cow manure slurry ha^{-1} to each of the five experimental plots.

Table 1 summarizes sampling times and additional analyses performed. The manure-40, manure-160, and fertilizer-80 plots were sampled for dissolved heavy metal analysis two times before the cow manure slurry treatment and four times after manuring. The manure-80 and manure-40 plots were sampled one time to perform metal speciation analyses (described below).

Soil Sampling

Samples were collected at depths between 0 and 80 cm, typically after a rainy period using a 3-cm diam., stainless steel motorized coring device. A preliminary study showed no difference in metal concentrations in soil samples between using the stainless steel device and a C-steel sampler.

During each sampling, 40 regularly-spaced core samples were taken from directly above the tile drain along the entire length of each plot (each subsample from plot 5 (Table 1) in April 1989 comprising 30 core samples). Core samples were grouped into seven depth intervals (0–20, 20–30, 30–40, 40–50, 50–60, 60–70, and 70–80 cm), then the 40 (or 30) samples of each depth interval were mixed to obtain one field sample representative for the depth interval.

The composited samples were stored in plastic bags at 4 °C until further use. A portion of each sample from the February 1989 sampling date was air dried at 40 °C for the determination of hot-acid-extractable metal concentrations.

Soil Solution Extraction

To determine metal solubilities, soil solutions were extracted from $\approx 100 \text{ cm}^3$ field moist soil samples by centrifugation at $2039 \times g$ using an extraction cup similar to that described by Edmunds and Bath (1976). Ross and Bartlett (1990) showed that increasing the relative centrifugal force from 390 to 2400 N kg^{-1} resulted in an increase of F, Cl, and SO_4 in the soil solution samples. In our study high forces were applied. In the centrifuge tube, the solution was expelled through a nonacid MN680M filter paper (Machery and Nagel Co., Düren) with a 6- μm nominal pore diameter and supported on a rigid plastic (Delrin) support. To separate larger or higher-density particles from soil solution, selected samples were supercentrifuged at 400 000 N kg^{-1} for 1 h (Table 1), then reanalyzed for heavy metal concentrations.

Solution samples for Cd and Cu speciation measurements by differential pulse anodic stripping voltammetry (DPASV) and by Chelex ion exchange resin (Bio-Rad Laboratories, Richmond, CA; Table 1) were obtained by preparing water saturation extracts (Rhoades, 1982) from field-moist samples from 0- to 10-, 10- to 20-, and 20- to 30-cm depth. The extracts were additionally filtered through a cellulose- NO_3 membrane filter with a nominal 0.45- μm pore diam.

Soil-solution samples were stored frozen in acid- and high-purity water washed polypropylene vials. Portions of the solutions used for heavy metal analyses were acidified to pH 1.6 with HNO_3 (Merck, Darmstadt, Germany; Suprapur), then stored in the dark at 4 °C until analyzed. Twelve hours prior to ana-

Table 1. Summary of sampling times, climatic conditions, and sample analyses.

Sampling no.	Sampling date	Mean soil moisture content† ($\text{m}^3 \text{ m}^{-3}$), and [% pore volume]	Mean temperature (°C)‡	Plots sampled§					Special analyses (comments)*
				1	2	3	4	5	
1	15 Feb. 1988	0.23 ± 0.02 [58]	4	x		x		x	
2	13 April 1988	0.24 ± 0.02 [60]	7	x		x		x	(Cattle slurry applied to all plots on 29 April 1988).
3	3 June 1988	0.16 ± 0.01 [40]	16	x		x		x	Metal analyses after supercentrifugation (60–80-cm depths).
4	10 Oct. 1988	0.25 ± 0.02 [63]	10		x		x		Cd and Cu speciation analyses (0–30-cm depths).
5	13 Dec. 1988	No data	6	x		x		x	Metal analyses after supercentrifugation (all plots and depths).
6	22 Feb. 1989	0.26 ± 0.02 [66]	5	x		x		x	Hot-acid-extractable soil Cd, Zn, Cu; supercentrifugation as Sampling 5.
7	11 April 1989	0.26 ± 0.05 [66]	6	x		x		x	3 subsamples from plot 5 analyzed; supercentrifugation as Sampling 5.
8	3 July 1989	0.22 ± 0.03 [56]	15	x		x		x	Soil particle-size distribution; total organic C; pH_{KCl}

† Calculated from measured gravimetric water contents and profile bulk density data (average bulk density for the profile was $1.6 \pm 0.1 \text{ Mg m}^{-3}$) for the Institute for Soil Fertility-Agricultural Research Department loamy-sand soil reported by Blaauw et al. (1988). Porosity calculated assuming particle density was 2.65 Mg m^{-3} .

‡ Mean ambient air temperature for the month of sampling (3 July 1989 data is mean of June 1989).

§ Plot treatments (see treatment code definitions in Materials and Methods section): Plot 1 = Manure-40; Plot 2 = Manure-80; Plot 3 = Manure-160; Plot 4 = Fertilizer-40; Plot 5 = Fertilizer-80.

Soil-solution samples analyses reported for all samplings except July 1989 (see Materials and Methods section for analyses performed).

lyzing the acidified samples by flame atomic absorption spectrometry (FAAS), concentrated HCl (Merck; Suprapur) was added to bring the final concentration to 6 M HCl.

Sample Analyses

Soil Samples

Hot-acid-extractable heavy metal analyses were performed on soils from the 15 Feb. 1988 sampling. Many analytical studies have shown that hot-acid-extractable heavy metal levels are equal to or only slightly lower than total heavy metal levels in the Netherlands. Total (soil) organic carbon (TOC), pH_{KCl} , and particle-size fractionation were performed on samples from 3 July 1989 (Table 1).

Heavy metal soil analyses were carried out in duplicate following the methods of Vierveijzer et al. (1979). To determine hot-acid-extractable Cd concentrations, 2 g of ground dry soil was digested in a borosilicate glass dish at 100 °C by addition of 10 mL concentrated HNO_3 and allowing the mixture to dry. Addition of acid and drying was done five times, and the dry residue was boiled with 4 mL concentrated HCl and 20 mL water. After cooling, filtering and bringing the volume to 200 mL, the pH was adjusted to 3 with sodium citrate in a separatory funnel; then acetyl acetone and 15 min later chloroform were added. The acetyl acetone-chloroform extraction (mechanical shaking) was repeated twice, and the organic phase containing Fe was discarded. After adding NH_4OH to the aqueous phase, to obtain a pH of 7, sodium diethyldithiocarbamate (NaDDC) and 4-methyl-2-pentanone (MIBK) were added, and the separatory funnel was shaken for 90 s. Cadmium was measured using FAAS in the organic phase (MIBK) after filtration.

To determine hot-acid-extractable Cu, Fe, and Zn concentrations, 1 g of soil was digested for ≈ 1 h using 30 mL of a boiling 4:1 (v/v) mixture of concentrated H_2SO_4 and HNO_3 , with repeated additions of 1 mL HNO_3 till white fumes remained visible. After boiling with 2 mL KCl solution (19.1 g L^{-1}), the digested residue was filtered and the filtrate was brought to 100 mL volume.

Cadmium, Cu, Fe, and Zn were measured in duplicate using a Perkin-Elmer Model 5000 flame atomic absorption spectrophotometer (Perkin-Elmer, Norwalk, CT).

Soil oxalate extractable Fe was determined following a method originating from the procedure of Tamm (1922). A 2.5 g air-dried soil sample was extracted in the dark with 50 mL 0.2 M ammonium oxalate-oxalic acid solution by gentle shaking for 2 h. The first 10 mL of the filtrate (MN640d nonacidic filter paper) were discarded and Fe was measured in the filtrate using spectrophotometry (Stookey, 1970).

For TOC determinations, the dichromate oxidation of air-dried soil samples was followed by back titration of residual dichromate (Mebius, 1960).

Soil clay (particles $< 2 \mu\text{m}$) content was measured by the pipette method (Vierveijzer et al., 1979). Particle size-fractions $< 16 \mu\text{m}$, 16 to $52 \mu\text{m}$, and $> 52 \mu\text{m}$ were determined in soil samples from four depths following the sieving and sedimentation procedure of Gee and Bauder (1986) where organic matter was removed from these samples by treatment with hydrogen peroxide.

Soil pH_{KCl} was determined after shaking 20 g (dry weight) of field-moist soil with 100 mL of 1 M KCl solution for 2 h, and gravitational settling of particles. The pH was measured in the supernatant solution with a glass-calomel electrode.

Soil-Solution Samples

Electrical conductivity, pH, and chemical oxygen demand (COD) were measured in freshly-centrifuged soil-solution samples. The COD was measured by the dichromate method and DOC (g C m^{-3}) was calculated from COD-values as mentioned for TOC. The EC was measured using a 1-cm cell

conductivity meter (El-Hama Instruments, Model TH27, Rosh pina, Israel) calibrated with standard KCl solutions and corrected for temperature. The pH was measured using the glass-calomel electrode.

In the acidified soil solution samples, Fe and Zn were analyzed using FAAS. Using standard additions and acid ammonium sulphate or nitric acid solutions as matrix modifiers, Cd and Cu were measured using electrothermal atomic absorption spectrometry (ETAAS) (Perkin Elmer, Model 5000, AS40). A certified river water reference sample for trace metals (SLRS-1, obtained from the National Research Council, Halifax, Nova Scotia, Canada) was periodically analyzed for quality control during the trace metal analyses.

Cadmium and Copper Speciation

An overview of the methods for the measurement of heavy metal speciation was given by Del Castilho (1991). Labile fractions of dissolved Cd and Cu were measured in nine selected (Table 1) water saturation extracts using both Chelex-resin cation exchange columns and DPASV combined with total dissolved concentration measurements (ETAAS). Both Chelex and DPASV methods were slightly modified from the methods for surface waters described in detail by Figura and McDuffie (1980). The exchange material was Ca-saturated Chelex packed in a 1.2-cm diam. polyethylene column with a polytetrafluoroethylene stopcock. The pore volume was $\approx 1.5 \text{ cm}^3$. A 250-mL portion of each filtered saturation-extract sample was eluted through the column at 3 mL min^{-1} using a peristaltic pump. Cadmium and Cu concentrations in influent and effluent samples were analyzed (ETAAS) as described above for soil solutions. Metal exchanged on the resin, calculated as the difference between influent and effluent concentrations, was considered to be bound in fast-dissociating (labile) complexes.

For the voltammetry experiments, membrane-filtered ($0.45 \mu\text{m}$) samples were buffered by mixing 4.0 mL of sample with 1.0 mL of 0.5 mol $\text{C}_2\text{H}_3\text{O}_2\text{Na L}^{-1}$ solution (pH 4.6) in the sample measurement vial. The instrumental procedures and settings on the PAR Model 174A polarograph (PAR Corp., Princeton, NJ) were (i) purging with 99.97% pure $\text{N}_2(\text{g})$ for 10 min, (ii) collecting at -650 mV potential for 30 s using a medium stirring speed, (iii) waiting for 15 s, and (iv) scanning at 5 mV s^{-1} with a pulse height of 50 mV. A PAR 303-A electrode with a medium Hg drop size was used. Peak heights were recorded and calibrated against peak heights of standard metal- NO_3 solutions containing the same buffer solution as used for samples.

In theory, the analytical results for Cd and Cu from a voltammetry experiment include the combined concentrations of free hydrated ions, ion pairs, and labile organic complexes (e.g., carboxylic group-metal salts). The time scale of voltammetry measurements at a hanging mercury drop is $\approx 0.2 \text{ s}$ for low molecular size complexes (Davison, 1978). Interpretation of experimental results is hampered by the possibility of sorption on the electrodes, and slow diffusion or slow complex dissociation kinetics. Sorption of stable metal complexes on the electrode surface, followed by direct reduction of the complex, would lead to an overestimation of the labile fraction. The high molecular weight of (slowly diffusing) metal complexes, even if extremely labile, would lead to an underestimation of the labile fraction.

For Chelex cation exchange experiments, the time scale was assumed to be equal to the residence time of the sample in the pore volume of the column: 30 s in our experiments. Any metal able to exchange at the column material within the time period was included in the labile pool. The interpretation of these results is hampered by the possibility of sorption on the column of stable metal complexes, thus leading to an overestimation of the labile fraction.

Ideally, both techniques can be used for the determination of free ions, ion pairs, and weak complexes. Because no sam-

Table 2. Total organic carbon (TOC), particle-size distribution, and pH_{KCl} for the experimental soil profile.

Depth (cm)	TOC† content g kg ⁻¹	Particle-size distribution‡				pH _{KCl} §		
		<2 µm† g kg ⁻¹	2–16 µm g kg ⁻¹	16–50 µm g kg ⁻¹	>50 µm g kg ⁻¹	Plot no.		
						1	3	5
0–20	22 ± 1	27 ± 4	30	125	818	5.0	4.7	5.5 ± 0.5
20–30	22 ± 1	27 ± 3	nd	nd	nd	4.9	4.7	5.3 ± 0.4
30–40	21 ± 3	25 ± 4	28	89	858	4.8	4.7	5.0 ± 0.1
40–50	13 ± 3	24 ± 5	7	98	871	4.7	4.8	5.0 ± 0.1
50–60	8 ± 2	24 ± 5	nd	nd	nd	5.0	4.8	4.7 ± 0.1
60–70	5 ± 1	21 ± 5	7	35	937	5.0	4.8	4.8 ± 0.1
70–80	4.2 ± 0.4	20 ± 5	nd	nd	nd	5.0	4.8	4.9 ± 0.1

† TOC and < 2-µm particle-size fractions represent means and standard deviations of five replications: one sample each from the manure-40 (Plot 1) and manure-160 (Plot 3) plots, and three subsamples from the fertilizer-80 plot (Plot 5).

‡ Particle-size fractions < 16, 16 to 50, and > 50 µm determined separately from the < 2-µm fraction on soil from the manure-40 plot; the 2 to 16-µm fraction proportion was calculated as the difference between the < 16-µm fraction and the reported mean of the < 2-µm fraction.

§ pH_{KCl} was measured in three subsamples from Plot 5; mean and standard deviation are given. Other results represent the mean of duplicate measurement.

ple-clean up to eliminate interferences is done, the analytical results are a priori unreliable. Therefore the two fundamentally different techniques were applied, assuming reliable results were obtained if the results agreed within certain limits.

RESULTS AND DISCUSSION

Soil Properties

Soil physical and chemical properties are summarized in Tables 2 and 3. A statistical analyses of the data in Table 2 by multiple comparisons (Tukey's *w* procedure) showed (i) no significant differences in pH_{KCl} between different soil profile layers, (ii) significant differences (99% level) in TOC content between (but not within) the 0- to 40-cm, 40- to 50-cm, and 50- to 80-cm layers, and (iii) no significant differences in clay content between layers or sample intervals.

Even without performing statistical analysis (a small data set) on the data in Table 3, the following general trends in hot-acid-extractable soil heavy metal concentrations are apparent: (i) soil Cd, Cu, and Zn typically decreased with increasing depth, (ii) soil Cd between 0 and 40 cm tended to vary between plots in the order fertilizer-80 > manure-160 > manure-40, (iii) soil Cu and Zn between 0 and 40 cm tended to vary between plots in the order manure-160 > manure-40 > fertilizer-80, and (iv) the variability of oxalate-extractable Fe increased with increasing depth.

The differences in concentrations were in accordance with the known elevated Cd content of phosphate fertilizers and the previously elevated amounts of Cu and Zn in pig-manure slurry.

Temporal Variations in Heavy Metal Solubilities

The variation for each dissolved heavy metal concentration in the various field plots is shown in Fig. 1 a through 1f. The data represent the average concentrations within layers having a significant difference in TOC (0–40 cm; 40–50 cm, and 50–80 cm). Similarly, mean pH values, DOC, and EC data are shown in Fig. 2 a through 2i. The sampling dates are coded with numbers 1 through 7. Some standard deviation values (Fig. 1 and 2) are shown.

Sampling 3 was done 6 wk after the application of cattle-manure slurry on top of the plots. The impact of recent manure slurry application on the Cd and Zn concentrations in the topsoil is shown in Fig. 1. Topsoil dissolved Cd and Zn concentrations both were significantly higher ($P < 0.01$) in the manure-40 and -160 plots when compared with the rest of the season: Zn (up to 33 mmol m⁻³, as compared with 0.46 to 3.2 mmol m⁻³ for the other samplings) and Cd (up to 0.09 mmol m⁻³, as compared with 0.0027 to 0.013 mmol m⁻³). These incidentally high concentrations found at 0- to 20-cm, or 20- to 30-cm depth coincided with an ≈ 10-fold increase in EC and one pH unit decrease for the soil solution (Fig. 2a and 2c). The fertilizer-80 plot (with the highest soil Cd level of all topsoil study plots) showed the lowest soil solution Cd concentration. The reason for this seemed to be the significantly higher soil solution pH of 5.3 vs. a pH of 4.8 or 4.5 for the manure-40 and -160 plots (20–30 cm values). In general, Cd adsorption increases with pH (e.g., Christensen, 1984), supporting this explanation.

Table 3. Hot-acid-extractable Cd, Cu, and Zn; and oxalate-extractable Fe for the experimental soil profile.

Depth (cm)	Acid-extractable soil metal content (mg kg ⁻¹)†														
	Manure-40					Manure-160					Fertilizer-80				
	Cd	Cu	Zn	Fe _{ox}	(CV %)	Cd	Cu	Zn	Fe _{ox}	(CV %)	Cd	Cu	Zn	Fe _{ox}	(CV %)
0–20	0.10	11	15	887	(9)	0.11	26	21	950	(6)	0.16	7.5	12	974	(4)
20–30	0.09	11	15	921	(12)	0.12	26	21	929	(5)	0.15	7.5	15	978	(4)
30–40	0.07	7.5	12	943	(14)	0.05	7.4	12	832	(10)	0.13	3.7	10	765	(10)
40–50	0.03	3.7	7.6	1125	(21)	0.04	3.7	6.9	925	(25)	0.03	3.7	10	831	(24)
50–60	0.01	1.0	5.3	1105	(23)	0.01	3.7	5.3	824	(21)	0.01	3.7	4.6	789	(21)
60–70	0.003	3.7	3.0	982	(37)	0.003	3.7	4.6	809	(31)	0.01	1.0	4.6	816	(14)
70–80	0.003	1.0	3.0	733	(34)	0.003	3.7	4.6	737	(39)	0.003	1.0	3.8	712	(14)

† Cadmium, Cu, and Zn by hot acid extraction [coefficient of variation (CV) was 10–15%]; Fe by oxalate extraction (see Materials and Methods section for procedure details). All measurements are on an air-dry soil basis.

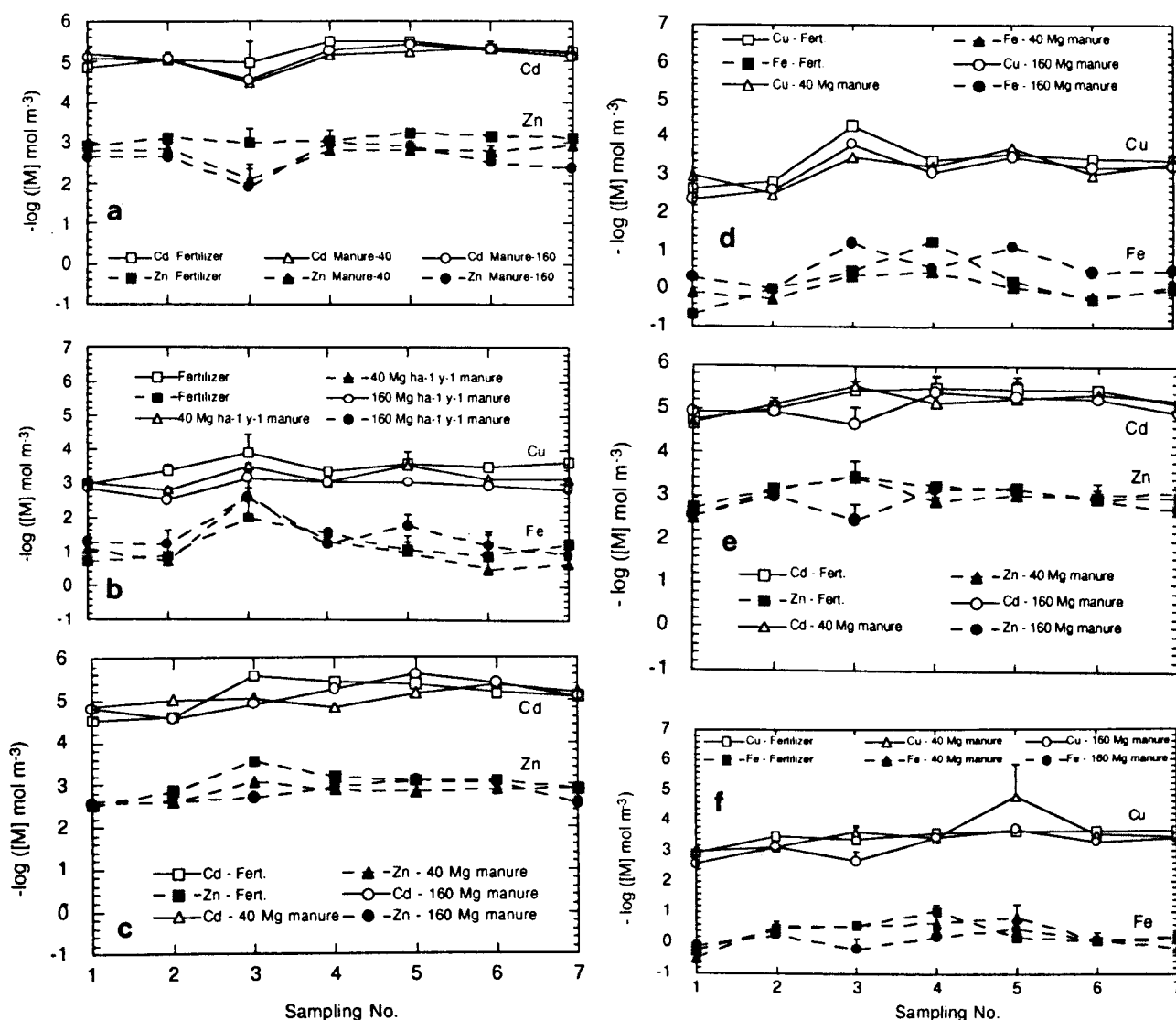


Fig. 1. Overview of the heavy metal concentrations (mean negative logarithm values; analogue with pH values) in the soil solution from Sampling 1 to 7, February 1988 to April 1989. In the 0- to 40-cm layer for three plots: (a) Cd and Zn; and (b) Cu and Fe. In the 40- to 50-cm layer: (c) and (d). In the 50- to 80-cm layer: (e) and (f).

tion. Differences in EC between the plots were not statistically significant. Copper and Fe concentrations in the top layer solutions were not significantly affected.

In the subsoil, elevated Zn, Cd, and Cu concentrations were found in the manure-40 and -160 plots together with elevated Fe and DOC concentrations. The low EC values indicated that the manure slurry salt front had not reached these layers.

Supercentrifugation was applied to soil solution samples from the manure-160 plot. About 90% of the heavy metals and Fe, and 79% of the DOC were removed. Thus, 21% of DOC, 5 to 15% of Cu and 5 to 20% of Cd and Zn remained in solution. In other samplings, December 1988 and April or July 1989, as much as 50 to 80% of the DOC (mean 60%), 90 to 100% of Cd and Zn, $\approx 75\%$ of the Cu, and 24% of the Fe remained in solution after supercentrifugation. The cause of the higher solution concentrations was not clear. Anaerobic dissolution of oxides from the soil layers seemed probable. The fact that a large percentage of the solutes obviously consisted of larger, or higher density, colloids supported

this hypothesis. No precautions were taken in the laboratory to maintain anaerobic conditions in the samples, and the oxidation of Fe(II) to insoluble Fe(hydr)oxides may have occurred.

The apparent association of heavy metals with dissolved organic material was studied with multiple linear regression analysis using the stepwise variable selection mode of the program Statgraphics, Version 4.0, (STCT). All individual data were taken together to determine the extent of correlation between dissolved Cd, Cu and Zn (mol m^{-3}), and pH, DOC (g C m^{-3}), Cd_{soil} , Cu_{soil} , and Zn_{soil} (hot-acid-extractable metals, mg kg^{-1} dry soil), oxalate extractable Fe (Fe_{ox} , mg Fe L^{-1} extract), TOC (mg C kg^{-1} dry soil), and EC ($\mu\text{S cm}^{-1}$). The resulting regressions with highly significant parameter coefficients ($P \leq 0.01$) were:

$$\begin{aligned} \log \text{Cd} = & -15.3 - 0.74 \text{ pH} + 0.70 \log \text{DOC} \\ & + 0.28 \log \text{EC} + 0.46 \log \text{Fe}_{\text{ox}}; \quad [1] \\ (r^2 = & 0.52 \text{ (adj. for d.f.)}; n = 105) \end{aligned}$$

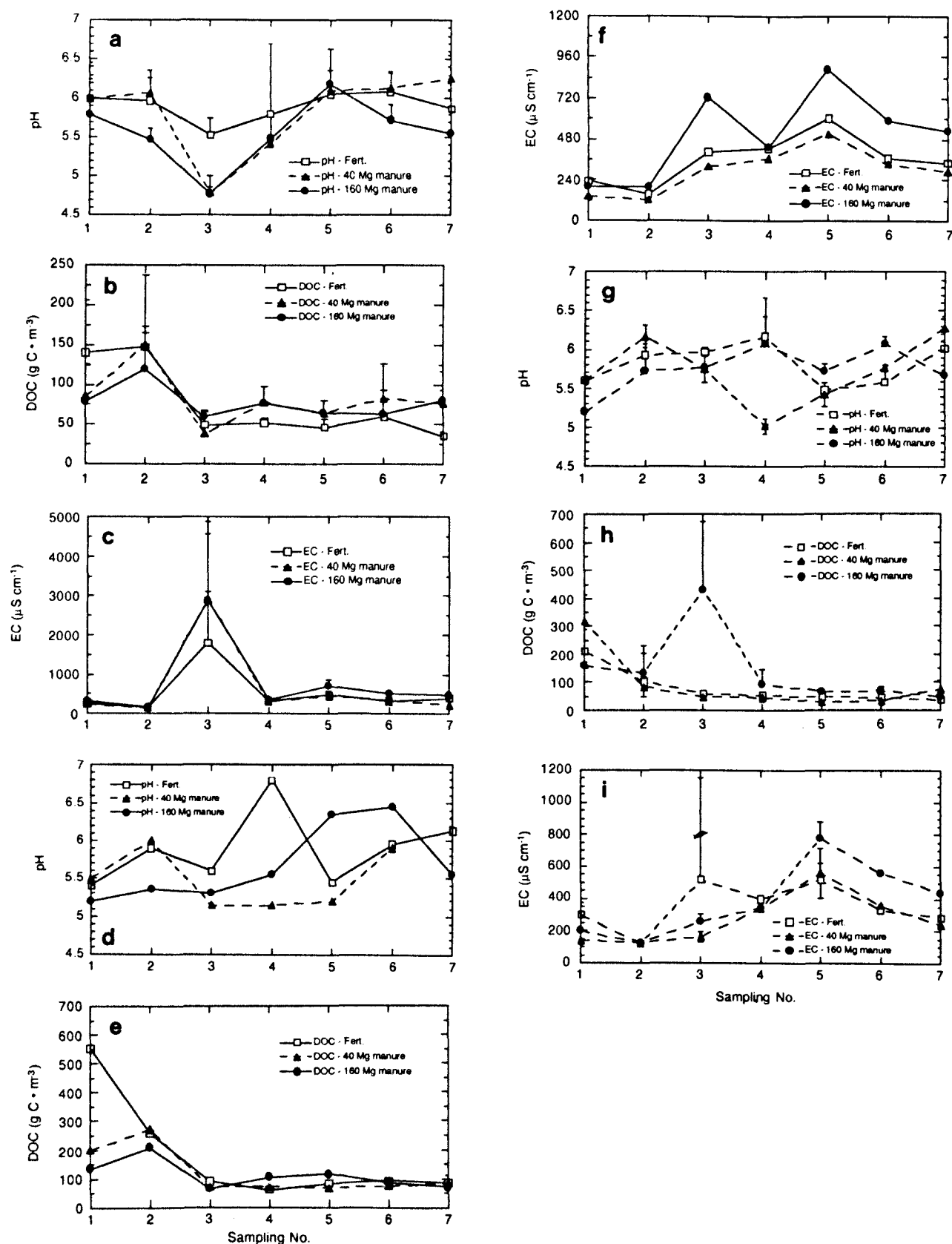


Fig. 2. Overview of pH, dissolved organic C (DOC), and electrical conductivity (EC) in the soil solution from February 1988 to April 1989. Results are shown for 0- to 40-; 40- to 50-; and 50- to 80-cm depth.

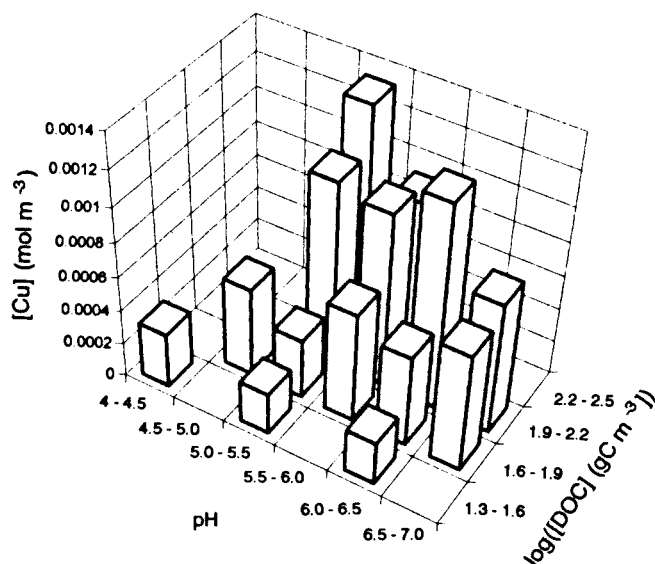


Fig. 3. Three-dimensional pH-Log [dissolved organic C (DOC)]-[Cu] diagrams for topsoil.

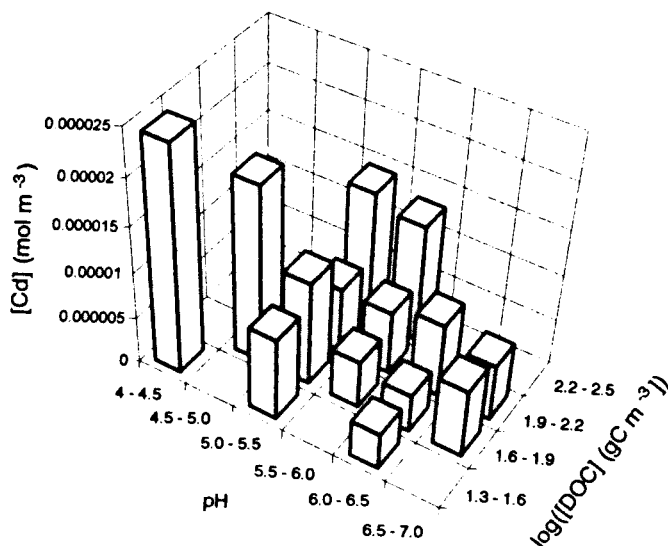


Fig. 4. Three-dimensional pH-Log [dissolved organic C (DOC)]-[Cd] diagrams for topsoil.

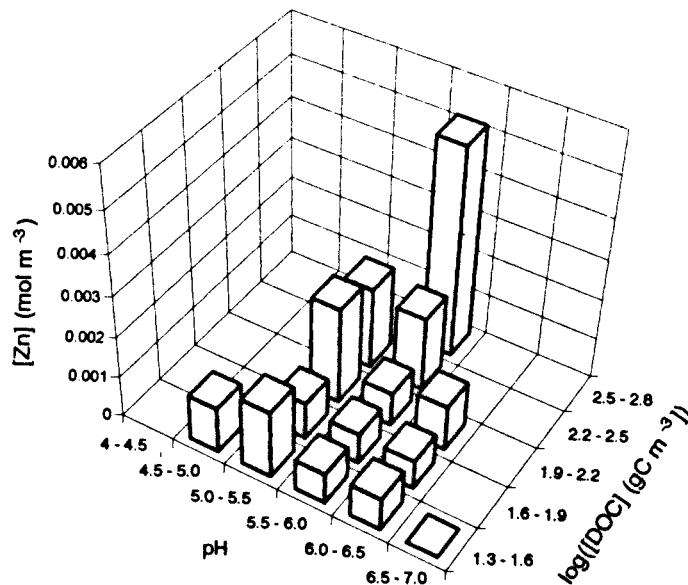


Fig. 5. Three-dimensional pH-Log [dissolved organic C (DOC)]-[Zn] diagrams for subsoil.

centrations. The regressions included the extreme EC values collected during Sampling 3. When the data from Sampling 3 were excluded from the regression analysis, DOC, EC, Cu_{soil} , and TOC were significant variables accounting for variations of Cu in solution. Excluding Sampling 3, the EC did not significantly influence Cd and Zn: pH, DOC, and TOC (and Zn_{soil} for Zn) were significant parameters. This result suggested that for Cd and Zn, the effect of EC was important only when it was highest (after manuring).

Multiple regressions were also constructed using the data grouped in sampling intervals according to soil organic matter content (as above): top layer (0–40 cm), intermediate layer (40–50 cm), and sublayer (50–80 cm). The general trends of metal solubilities with pH and DOC are shown in three-dimensional plots (Fig. 3, 4, and 5). Here [Cu] and [Cd] for the top layer, and [Zn] for the sublayer are shown (metal concentrations expressed in $mol\ m^{-3}$). The backtransformed mean of the logarithmic values are shown. Consistent with the regressions of the overall set, Cd, Cu, and Zn concentrations tended to increase with increasing DOC and decreasing pH.

In the top layer and in the sublayer, both pH and DOC were significant variables accounting for Cd and Zn variations; in the top layer, pH, and in the sublayer, DOC, was the most significant variable.

In the intermediate layer, pH and DOC were also both significant, but in contrast with top- and sublayers, Cd and Zn concentrations decreased with increasing EC (data set without sampling 3). In general, it is to be expected that an increase in EC promotes the dissolution of Cd and Zn from the soil surface (García-Miragaya and Page, 1976). The observed opposite effect in the intermediate layers could have been related to a decrease in DOC solubility at high I and a subsequent lowering of DOC-promoted dissolution of Cd and Zn.

Copper correlated positively with DOC in all sublayers, and as with Cd and Zn (see above), negatively with EC in the intermediate layers. In other layers there was no significant correlation between Cu and EC.

$$\begin{aligned} \log Zn = & -7.47 - 0.86\ pH + 0.57\ \log DOC \\ & + 0.31\ \log EC + 0.91\ \log Zn_{soil} + \\ & - 0.53\ \log TOC; \end{aligned} \quad [2]$$

$$(r^2 = 0.59\ (\text{adj. for d.f.});\ n = 105).$$

$$\begin{aligned} \log Cu = & -10.0 + 0.89\ \log DOC - 0.36\ \log EC \\ & + 0.47\ \log Cu_{soil}; \end{aligned} \quad [3]$$

$$(r^2 = 0.49\ (\text{adj. for d.f.});\ n = 107);$$

where d.f. means degrees of freedom and n is the number of observations.

These regressions suggested that the soil solution DOC and EC consistently influenced the concentrations of Cd, Cu, and Zn; in addition, pH influenced Cd and Zn con-

Taking into account the dependence of the behavior of Cd and Zn on pH and DOC could be useful for developing regulations and standards for metal pollution. However, present Dutch soil pollution standards (Guideline Soil Sanitation, 1988) regard clay and organic matter content but disregard pH and DOC.

Despite the significant correlations between DOC and heavy metal concentrations, large variations in metal to DOC ratios were found: coefficients of variation ($100\% \times \text{standard deviation/mean value}$) for the Cd, Cu, and Zn/DOC ratios, with and without Sampling 3, were: 150% (50%); 90% (88%); and 195% (76%) respectively. Differences in the nature (complexing affinity) of the DOC may have been a cause of variation. The role of DOC in complexing Cd and Cu was assessed in more detail by cation exchange and voltammetry study.

Labile Fraction of Dissolved Cadmium and Copper Complexes

The results obtained with the two speciation techniques showed a fair degree of agreement for Cd and Cu. Cadmium was found to be labile in all nine samples with both methods, and was probably bound in fast-diffusing, fast-dissociating complexes. Hence, a negligible part of the Cd would be expected to be associated with high-molecular weight DOM. The labile fraction of Cu varied from ≈ 30 to $\approx 70\%$ in both methods (Fig. 6). A considerable part of the Cu was found in higher molecular weight or slowly dissociating (nonlabile) complexes. Because a systematically greater labile fraction was measured with voltammetry than with ion-exchange (Fig. 6), especially at low Cu concentrations, it seemed likely that the nonlability was the result of slow dissociation kinetics of complexes, rather than of low diffusion velocity by a high molecular weight. However, a partial penetration of high molecular weight complexes into the gel

(Chelex) might as well explain the observed systematic differences. Del Castilho et al. (1993) found for gel permeation fractions of animal manure slurry-soil incubates, that all Cd and Zn, and only a part of the soil solution Cu complexes dissociated within 120 h of contact with Chelex in batch extraction experiments. The nonlabile behavior was attributed to slow dissociation kinetics because of the calculated high Cu complex stability.

The observed lability of Cd complexes supported the assumption of an immediate chemical reaction of Cd with strong binding sites of soil solids, or biological surfaces, and components in the soil solution. The nonlabile Cu complexes to a large extent can be considered as molecules that do not behave as a metal but as a ligand. Such molecules would be expected to show different partition over dissolved and solid phase than the aqueous Cu ion. Extremely strong binding sites would be needed to strip Cu from the nonlabile dissolved copper complexes. Only the fast-dissociating (labile) portion of the Cu complexes would supply the soil solution with appreciable amounts of Cu ions which show a metal behavior towards soil and biological surfaces.

CONCLUSIONS

Temporal variations of heavy metal concentrations in soil solutions during seven sampling events during an 18-mo period (1988–1989) showed that the application of dairy cattle-manure slurry increased Cd and Zn concentrations by an order of magnitude in historically manured topsoils. Multiple regressions ($0.48 < r^2 < 0.59$) suggested that the following soil solution parameters, in order of importance, increased Cd and Zn concentrations: low pH, high DOC, and high EC-levels. Copper concentrations increased with increasing DOC only. In the intermediate soil layer, Cd, Cu, and Zn were all negatively correlated with EC.

The occasionally strongly elevated DOC and soil solution metal concentrations in the subsoil both were substantially lowered by supercentrifuging, suggesting an association between the metals and colloids.

The results of cation exchange and DPASV experiments with nine membrane filtrated topsoil saturation extracts, all from the same sampling date, indicated that Cd and Cu are found in lower molecular weight complexes. All Cd, and 30 to 70% of Cu were bound in fast-dissociating complexes.

Concentrations of heavy metals in the soil solution were highly influenced by pH, DOC, EC, and TOC.

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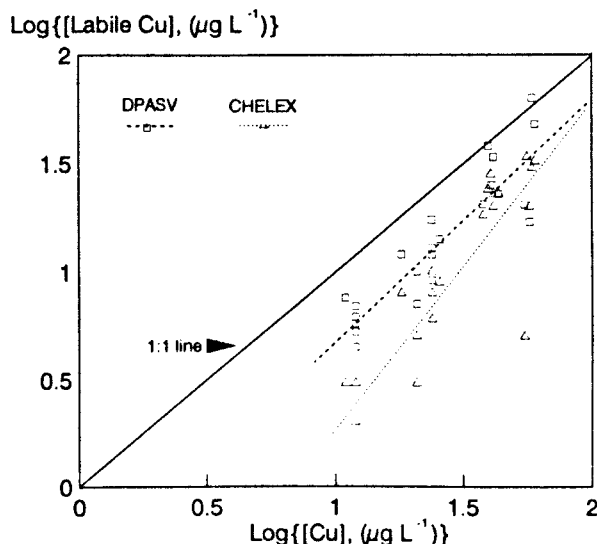


Fig. 6. Labile copper concentrations are shown as a function of the Cu concentration in top layer soil saturation extracts. Copper concentration was measured with electrothermal atomic absorption spectrometry (ETAAS) and labile Cu with two techniques: differential pulse anodic stripping voltammetry (DPASV) and Chelex. Both regression lines are shown.

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